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(71) Applicant (for all designated States except US): THE PROC-TER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and
(75) Inventors/Applicants (for US only): BAKER, Keith, Homer [US/US]; 10083 Bennington Drive, Union Township, OH 45241 (US). KLEINSTEUBER, Ulrich [DE/BE]; Tangedallaan 17, bus 5, B-1850 Grimbergen (BE). HARTSHORN, Richard, Timothy [GB/GB]; 139 Dene Road, Wylam, Northumberland NE41 8EY (GB). MORINI, Massimo

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

[IT/BE]; Italielaan 6A, B-3090 Overijse (BE).

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(57) Abstract

A hydrophobic bleaching agent comprising a peroxyacid having a carbon chain of at least 9 carbon atoms is used for the reduction of the activity of micro-organisms which have a cell wall containing high levels of peptidoglycan. These include yeast and in part icular gram positive bacteria.

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WO 00/15750 PCT/US99/21166

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Sanitising Compositions and Methods

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Technical Field

This invention provides methods for improved sanitisation and the use of specific sanitising compositions.

Background to the Invention

Traditionally, hard-surface cleaners contain bleach as cleaning agent and as disinfectant.

In particular, they contain high levels of chlorine bleach to achieve the required cleaning and disinfecting properties.

Research has shown that hydrogen peroxide bleach in laundry and dish washing

detergents also has a disinfecting action, see for example M Blaser et al. in: The journal of infectious diseases, vol 149, no.1,1984.

More recently, detergent manufacturers have become interested in the disinfecting properties of these detergents. Various disclosures describe bleach systems which provide both cleaning and disinfecting during the laundering, for example DE 19616782, DE19605688, DE 19536082, WO9418297. Not all bleach systems which have disinfecting properties are suitable for detergents: they are not always compatible with other detergent ingredients, such as enzymes, or the levels of bleach required to obtain disinfecting are too high and may damage the fabrics.

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The inventors now have found that most bleach systems known in the art, including TAED, percarbonate and perborate bleaches, effectively kill gram negative bacteria, but

not effectively other micro-organisms, in particular, gram all positive bacteria. Also, it has been found that the anti-bacterial activity of for example TAED is dependent on the pH, resulting in a strong reduction of anti-bacterial activity on gram positive bacteria at a alkaline pH, such as for example during washing conditions.

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Many soils, including body soil, mainly contain micro-organisms other than gram negative bacteria, in particular, gram positive bacteria. The inventors have found that detergents containing for example TAED and a peroxygen source do thus not effectively sanitise these types of soils, in particular at low temperatures as normally used by consumers during laundering, dish washing or other cleaning methods.

They have now found that specific hydrophobic bleaching agent effectively inactivate micro-organisms including gram positive bacteria, such as Enterococcus hirae and Staphyloccocus aureus bacteria. Thus, when these specific hydrophobic bleaching agents are used in detergents, not only excellent stain removal of bleachable stains and soils is achieved but also sanitisation.

It is believed that the specific hydrophobic bleaching agent have an improved surface activity for the peptidoglycan in the cell walls of, for example, yeast and gram positive bacteria, compared to hydrophilic bleaching agents. It is believed that these specific hydrophobic agents thus penetrate and disrupt these cell walls more effectively than other hydrophilic bleaching agents.

Since the specific hydrophobic bleaching agent is found to be very effective, a further benefit can be that reduced levels of bleach can be employed.

Further improved sanitisation can be achieved when both hydrophilic and hydrophobic bleaching agents are employed, resulting in effective inactivation of both gram positive bacteria and gram negative bacteria.

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Summary of the Invention

The invention provides the use of a hydrophobic bleaching agent comprising a peroxyacid having a carbon chain of at least 9 carbon atoms for the reduction of the activity of microorganism which have a cell wall which contain a high level of peptidoglycan.

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When used herein, 'high levels of peptidoglycan' means that the micro-organisms have high levels of peptidoglycan, compared to gram negative bacteria. The cell walls preferably comprise a layer which predominantly comprises peptidoglycan They include yeast and in particular, gram positive bacteria.

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When used herein, 'reduction of the activity of the micro-organisms' includes a reduction of the activity as defined in the CEN method prEN1276, 1993, (Comité Européen de Normalisation) and CEN method prEN 1650. The reduction therein is preferably represented by a reduction of micro-organisms, preferably at least of 10⁵, more preferably at least 10⁶ or even more for bactaria, or at least 10⁴ or even at least 10⁵ for yeast..

The reduction of the activity of the micro-organisms when used herein includes the reduction of any of the processes conducted by the micro-organisms which have a cell wall including high levels of peptidoglycan, compared to gram negative bacteria., including secretion of products but preferably the growth of the micro-organisms.

The invention also provides a method for reduction of the activity of micro-organisms, or preferably gram positive bacteria comprising the steps of contacting the micro-organism with an aqueous liquor comprising a hydrophobic bleaching agent comprising a peroxyacid having a carbon chain of at least 9 carbon atoms at a level of at least 100 ppm in the liquor, per 106 micro-organisms.

Detailed Description of the Invention

30 Method and Use

WO 00/15750 PCT/US99/21166

The specific hydrophobic bleaching agents herein are used to reduce the activity of specific micro-organisms which have high levels of peptidoglycan in the cell walls, including yeast and gram positive bacteria. In particular, this is done during a sanitisation process or a cleaning process. Hereby, the bleaching agent can be contacted with the specific micro-organisms in solid form, but preferably the bleaching agent is present in a liquor in contact with the micro-organisms.

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The specific micro-organisms gram positive bacteria can be present on the surfaces or fabrics to be cleaned and sanitised, for example on the fabrics to be cleaned in a dish washing process or laundry process. The gram positive bacteria can also be present in the liquor used for the cleaning or sanitisation process or in the equipment used in the process, such as the washing machine.

The micro-organisms having cell walls comprising relatively high levels of

peptidoglycan, in particular the gram positive bacteria, can be present in soils present on
these fabrics or surfaces, in particular in body soils.

The amount of hydrophobic bleaching agent required to obtain effective reduction of the activity of the specific micro-organisms, such as , yeast and gram positive bacteria depends on various factors, such as the amount of micro-organisms present, the conditions of the sanitisation or cleaning process, including the other compounds present, the temperature.

It should be noted that the present hydrophobic bleaching agent may also reduce the activity of micro-organisms which do not comprise high levels of peptidoglycan in their cell walls to a lesser extent, or less efficiently, e.g. gram negative bacteria.

In the method of the invention, the liquor used preferably comprises at least 100 ppm of the hydrophobic peroxyacid per 10⁶ micro-organisms, more preferably at least 200 ppm or even 250 ppm.

The reduction of the activity of the specific micro-organisms, having a peptidoglycan-containing cell walls can be determined by the Petrocci and Clarke method, as described in JOAC 1981, but is preferably determined for the purpose of this invention by the CEN method prEN1276, 1993 for bacteria and CEN method prEN1650 for yeast.

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Such a CEN method involves, for example, the preparation of gram positive bacterial inocula conform the DEN method, pages 7 and further, preparation of a solution comprising the hydrophobic bleaching agent at a level of about 250ppm, conducting the test following the CEN method, incubation TSA plates for 24 hours at 36°C;

and subsequently counting of the bacteria colonies on the plates.

This is compared with the results of the reference and the reduction of bacteria growth is calculated, for the defined contacting time.

15 Micro-Organisms

The specific micro-organisms herein comprise a cell wall which contain cell walls with high levels of peptidoglycan. In particular, useful herein are yeast and most preferably gram positive bacteria.

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The gram positive bacteria are typically present in soils on the fabric, in particular body soils. Typical gram positive bacteria are Enterococcus hirae and Staphyloccocus aureus.

Hydrophobic Bleaching Agent

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The hydrophobic bleaching agent herein comprises a peroxyacid having a carbon chain of at least 9 carbon atoms. The agent can be a preformed peroxyacid or it can be a compound which provides such a hydrophobic peroxyacid by a chemical reaction, such as the bleach precursors described herein. Also mixtures of these precursor and preformed hydrophobic peroxyacid can be used.

Preferably the hydrophobic bleaching agent comprises a hydrogen peroxide source and a hydrophobic peroxyacid bleach precursor. The production of the hydrophobic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide source. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches, described hereinafter.

The hydrophobic peroxyacid contains at least 9 carbon atoms, most preferably at least 11 carbon atoms. In a preferred aspect the peroxyacid has an alkyl chain, containing at least 8 or 9 or even at least 10 carbon atoms. Preferably, the peroxy acid but in particular the peroxy acid precursor comprises a N-acyl group.

Preferably, the hydrophobic peroxyacid bleaching agent in a solution is used to reduce the activity of gram positive bacteria, in particular in dish washing or laundry process such that the solution comprises at least 100 ppm of the peroxyacid or peroxyacid precursor per 10⁶ bacteria.

The precursors have a structure

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hereinafter L is a leaving group which must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

25 The L groups are preferably selected from the group consisting of:

also suitable as L group may be

$$-O-CH=\dot{C}-CH=CH_{2} \qquad -O-CH=\dot{C}-CH=CH_{2}$$

$$0 \qquad \qquad CH_{2}-\dot{C} \qquad NR^{4}$$

$$-O-\dot{C}-R^{1} \qquad -N-\dot{C}-NR^{4}$$

$$-O-\dot{C}=CHR^{4} \quad , \text{ and } \qquad -N-\dot{S}-CH-R^{4}$$

$$R^{3} \qquad 0$$

and mixtures thereof, wherein R¹ is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R³ is an alkyl chain containing from 1 to 8 carbon atoms, R⁴ is H or R³, and Y is H or a solubilizing group. Any of R¹, R³ and R⁴ may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammmonium groups

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The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<--N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$

wherein R³ is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Suitable hydrophobic peroxyacid bleach precursors herein typically contain one or more

N- acyl groups, which precursors can be selected from a wide range of classes. Suitable
classes include imides, lactams and acylated derivatives of imidazoles. Suitable Nacylated precursor compounds of the lactam class disclosed generally in GB-A-955735.

Preferred materials of this class comprise the caprolactams.

Highly preferred peroxyacid precursors are amide substituted alkyl peroxyacid precursor compounds, including those of the following general formulae:

wherein R¹ is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R¹ preferably contains from about 6 to 12 carbon atoms. R² preferably contains from about 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². R² can include alkyl, aryl, wherein said R² may also contain halogen, nitrogen, sulphur and other

typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

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A preferred class of hydrophobic organic peroxyacid compounds are the amide substituted compounds of the following general formulae:

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wherein R¹ is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms, provided that at least 9 carbon atoms are present. R¹ preferably contains from about 6 to 12 carbon atoms, preferably 9 to 12. R² preferably contains from about 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². R² can include alkyl, aryl, wherein said R² may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386. Suitable examples of this class of agents include (6-octylamino)-6-oxo-caproic acid, (6-nonylamino)-6-oxo-caproic acid, (6-decylamino)-6-oxo-caproic acid, magnesium

monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S. 4,634,551, EP 0,133,354, U.S. 4,412,934 and EP 0,170,386. A preferred hydrophobic preformed peroxyacid bleach compound for the purpose of the invention is monononylamido peroxycarboxylic acid.

Other suitable organic peroxyacids include diamino peroxyacids, which are disclosed in WO 95/ 03275, with the following general formula:

wherein

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R is selected from the group consisting of C_1 - C_{12} alkylene, C_5 - C_{12} cycloalkylene, C_6 - C_{12} arylene and radical combinations thereof;

 R^1 and R^2 are independently selected from the group consisting of H, C_1 - C_{16} alkyl and C_6 - C_{12} aryl radicals and a radical that can form a C_3 - C_{12} ring together with R^3 and both nitrogens; R^3 is selected from the group consisting of C_1 - C_{12} alkylene, C_5 - C_{12} cycloalkylene and C_6 - C_{12} arylene radicals; n and n' each are an integer chosen such that the sum thereof is 1; m and m' each are an integer chosen such that the sum thereof is 1; and M is selected from the group consisting of H, alkali metal, alkaline earth metal, ammonium, alkanolammonium cations and radicals and combinations thereof; and provided that the peroxyacid comprises at least 9 carbon atoms;

Other suitable organic peroxyacids are include the amido peroxyacids which are disclosed in WO 95/ 16673, with the following general structure:

$$X-Ar-CO-NY-R(Z)-CO-OOH$$

in which X represents hydrogen or a compatible substituent, Ar is an aryl group, R represents $(CH_2)_n$ in which n=2 or 3, and Y and Z each represent independently a

substituent selected from hydrogen or an alkyl or aryl or alkaryl group or an aryl group substituted by a compatible substituent provided that at least one of Y and Z is not hydrogen if n = 3. The substituent X on the benzene nucleus is preferably a hydrogen or a meta or para substituent, selected from the group comprising halogen, typically chlorine atom, or some other non-released non-interfering species such as an alkyl group, conveniently up to C6 for example a methyl, ethyl or propyl group. Alternatively, X can represent a second amido-percarboxylic acid substituent of formula:-

$$---$$
CO $-$ NY $-$ R(Z) $-$ CO $-$ OOH

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in which R, Y, Z and n are as defined above.

MOOC-R1CO-NR2-R3-NR4-CO-R5COOM

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wherein R^1 is selected from the group consisting of C_1 - C_{12} alkylene, C_5 - C_{12} cycloalkylene, C_6 - C_{12} arylene and radical combinations thereof; R

Hydrogen Peroxide Source

Inorganic perhydrate salts are a preferred source of hydrogen peroxide.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula NaBO₂H₂O₂ or the tetrahydrate NaBO₂H₂O₂.3H₂O.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Hydrophilic Bleach

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In the method herein or in the compositions herein, a hydrophilic bleaching agent may be present in addition to the hydrophobic bleaching agent. A suitable hydrophilic bleaching agent is TAED.

Preferably the hydrophilic bleaching agent is present at a ratio to the hydrophobic peroxyacid from 1:5 to 5:1, more preferably from 1:3 to 3:1, most preferably from 1:2 to 2:1

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Detergent Compositions

The hydrophobic bleaching agent herein is preferably present in a detergent composition, when used to reduce the activity of micro-organisms.

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Thus, the reduction of the activity preferably takes place during a cleaning method, preferably a automatic or hand laundry or dish washing method, in particularly at low temperatures up to 60°C or even 45°C or even 30°C.

When the hydrophobic peroxyacid bleaching agent contains a peroxyacid bleach precursor, the precursor is typically present at a level of from 0.05% to 20% by, more preferably from 0.5% to 10% by weight, most preferably from 1% to 7% by weight of the composition. When the hydrophobic peroxyacid bleaching agent contains a preformed hydrophobic peroxyacid, the preformed peroxyacid is typically present at a level of from 0.05% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

The hydrogen peroxide sources, when present, are preferably incorporated in the compositions herein the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

The hydrophilic bleach, when present, may preferably be present at a level of from 0.5% to 12% by weight of the composition.

The detergent compositions herein may comprise any additional ingredients, commonly employed in detergents. The precise nature of these additional components, and levels of

incorporation thereof will depend on the physical form of the composition and the precise nature of the washing operation for which it is to be used.

The compositions preferably contain one or more additional detergent components selected from surfactants, effervescence sources, bleach catalysts, chelating agnets, bleach stabilisers, alkalinity systems, builders, phosphate-containing builders, organic polymeric compounds, enzymes, suds suppressors, lime soap, dispersants, soil suspension and anti-redeposition agents, soil releasing agents, perfumes, dyes, dyed speckles, brighteners, photobleaching agents and additional corrosion inhibitors.

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Laundry Washing Method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition containing the hydrophobic bleaching agent in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods. Dosage is dependent upon the particular conditions such as water hardness and degree of soiling of the soiled laundry. The pH of the washing liquor is typically above 7, preferably above 8.5 or above 9 or even 9.5.

The detergent composition may be dispensed for example, from the drawer dispenser of a washing machine or may be sprinkled over the soiled laundry placed in the machine.

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In one use aspect a dispensing device is employed in the washing method. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly know as the

"granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

Machine Dishwashing Method

5 Any suitable methods for machine dishwashing or cleaning soiled tableware.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a machine dishwashing composition herein. By an effective amount of the machine dishwashing composition it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

Claims

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- 1. Use of a hydrophobic bleaching agent comprising a peroxyacid having a carbon chain of at least 9 carbon atoms for the reduction of the activity of microorganisms which comprise a cell wall containing high levels of peptidoglycan, preferably yeast, gram positive bacteria or mixtures thereof.
- Use according to Claim 1, wherein the hydrophobic bleaching agent comprises a hydrophobic peroxyacid precursor and a hydrogen peroxide source, preferably a
 percarbonate salt.
 - 3. Use according to Claim 1 or 2, wherein the peroxyacid comprises an N-acyl group.
- 4. Use according to any of Claims 1 to 3, whereby the hydrophobic bleaching agent comprises a 6-(nonanamidocaproyl) oxybenzene sulphonate salt.
- Use according to any of Claims 1 to 4, whereby an additional hydrophilic bleaching agent, preferably TAED, is present for reduction of the activity of gram negative bacteria.
 - 6. Use according to any of Claims 1 to 5 for sanitisation of soiled fabrics or surfaces, preferably sanitisation of fabrics or surfaces.
- A method for reduction of the activity of micro-organisms containing a cell wall which contains high levels of peptidoglycan, preferably gram positive bacteria, comprising the steps of contacting the micro-organisms with an aqueous liquor comprising a hydrophobic bleaching agent comprising a peroxyacid having a carbon chain of at least 9 carbon atoms at a level of at least 100 ppm in the liquor, per 106 micro-organism.

- 8. A method according to Claim 7, wherein liquor comprises a detergent composition comprising a hydrophobic peroxy acid precursor, present in a detergent composition at a level of at least 1% by weight, preferably up to 10% by weight.
- 5 9. A method according to Claim 8 the method being a laundry method for cleaning fabrics, comprising the step of contacting gram positive bacteria present on the fabric.

trs. xtional Application No PCT/US 99/21166

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C11D3/48 C11D3/39 A01N37/16	
According to International Patent Classification (IPC) or to both national classification a	nd IPC
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Documentation searched other than minimum documentation to the extent that such de	ocuments are included in the fields searched
Electronic data base consulted during the international search (name of data base and	i, where practical, search terms used)
C. DOCUMENTS CONSIDERED TO BE RELEVANT	
Category * Citation of document, with indication, where appropriate, of the relevant	passagee Relevant to claim No.
P,X WO 99 13037 A (PROCTER & GAMBLE) 18 March 1999 (1999-03-18) abstract; claims 8,9; example 4	1-9
WO 94 18297 A (WARWICK INT GROUP) 18 August 1994 (1994-08-18) cited in the application abstract; example 3.7	1-3,5-9
X WO 93 01716 A (ECOLAB INC) 4 February 1993 (1993-02-04) claims 53,59,60; example 1; table I	1,6-9
A US 5 021 182 A (JENTSCH GUNTER) 4 June 1991 (1991-06-04) abstract; examples	1-3,5-9
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